

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2011280799 B2**

(54) Title
Method for synthesizing ammonia

(51) International Patent Classification(s)
C25B 1/00 (2006.01) **B01J 35/02** (2006.01)
B01J 27/24 (2006.01) **C01C 1/02** (2006.01)

(21) Application No: **2011280799** (22) Date of Filing: **2011.06.03**

(87) WIPO No: **WO12/011324**

(30) Priority Data

(31) Number	(32) Date	(33) Country
2010-163537	2010.07.21	JP

(43) Publication Date: **2012.01.26**

(44) Accepted Journal Date: **2015.02.26**

(71) Applicant(s)
Hitachi Zosen Corporation

(72) Inventor(s)
Hikazudani, Susumu;Mori, Takuma;Araki, Sadao

(74) Agent / Attorney
Griffith Hack, GPO Box 4164, Sydney, NSW, 2001

(56) Related Art
Grayer et al, "Electrochemical and photoelectrochemical reduction of molecular nitrogen to ammonia," J. Electroanalytical Chemistry, Vol 170 (1984), pp. 363-368
US 4240882

(12) 特許協力条約に基づいて公開された国際出願

(19) 世界知的所有権機関
国際事務局



(43) 国際公開日
2012 年 1 月 26 日(26.01.2012)

(10) 国際公開番号
WO 2012/011324 A1

- (51) 国際特許分類:
C25B 1/00 (2006.01) *B01J 35/02* (2006.01)
B01J 27/24 (2006.01) *C01C 1/02* (2006.01)
- (21) 国際出願番号: PCT/JP2011/062790
- (22) 国際出願日: 2011 年 6 月 3 日(03.06.2011)
- (25) 国際出願の言語: 日本語
- (26) 国際公開の言語: 日本語
- (30) 優先権データ:
特願 2010-163537 2010 年 7 月 21 日(21.07.2010) JP
- (71) 出願人(米国を除く全ての指定国について): 日立造船株式会社(HITACHI ZOSEN CORPORATION) [JP/JP]; 〒5598559 大阪府大阪市住之江区南港北 1 丁目 7 番 8 9 号 Osaka (JP).
- (72) 発明者; および
- (75) 発明者/出願人(米国についてのみ): 日数谷 進(HIKAZUDANI, Susumu) [JP/JP]; 〒5598559 大阪府大阪市住之江区南港北 1 丁目 7 番 8 9 号 日立造船株式会社内 Osaka (JP). 森 匠磨(MORI, Takuma) [JP/JP]; 〒5598559 大阪府大阪市住之江区南港北 1 丁目 7 番 8 9 号 日立造船株式会社内 Osaka (JP). 荒木 貞夫(ARAKI, Sadao) [JP/JP]; 〒5598559 大阪府大阪市住之江区南港北

1 丁目 7 番 8 9 号 日立造船株式会社内 Osaka (JP).

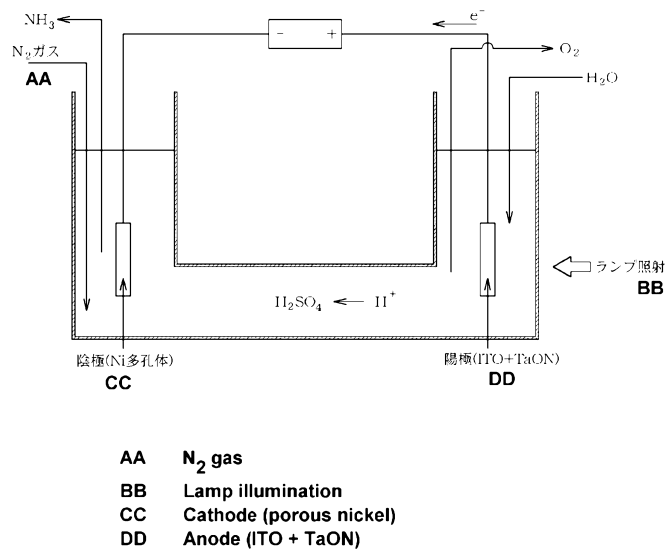
- (74) 代理人: 日比 紀彦, 外(HIBI, Norihiko et al.); 〒5420086 大阪府大阪市中央区西心斎橋 1 丁目 1 3 番 1 8 号 イナバビル 3 階 キシモト特許事務所内 Osaka (JP).
- (81) 指定国(表示のない限り、全ての種類の国内保護が可能): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) 指定国(表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), ユーラシア(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), ヨーロッパ(AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI

[続葉有]

(54) Title: METHOD FOR SYNTHESIZING AMMONIA

(54) 発明の名称: アンモニアの合成方法

[図1]



- AA N₂ gas
BB Lamp illumination
CC Cathode (porous nickel)
DD Anode (ITO + TaON)

(57) Abstract: The disclosed method for synthesizing ammonia can do so without using hydrogen gas. Said method does not use traditional hydrogen sources, namely fossil fuels such as natural gas, and thus avoids increases in ammonia manufacturing costs due to rising fossil-fuel prices and also avoids burdening the environment with carbon dioxide emissions. Furthermore, said method is performed at ordinary temperatures and pressures and thus can be performed by a small-scale facility that uses little energy, making the method highly economical. In the disclosed method, an anode and a cathode are arranged in an electrolyte phase at a prescribed separation. In an anode zone, water and light are supplied and the water is broken down by a light-absorption reaction, generating protons, electrons, and oxygen gas. In a cathode zone, nitrogen gas is supplied, the electrons generated in the anode zone are moved to the cathode zone via a wire lead, N³⁺ is formed in the cathode zone, and ammonia is synthesized via a reaction between said N³⁺ and protons that have moved from the anode

zone to the cathode zone side through the electrolyte phase.

(57) 要約:

[続葉有]



(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

添付公開書類:

— 国際調査報告 (条約第 21 条(3))

水素ガスを用いることなくアンモニアの合成が可能であり、従来の水素源としての天然ガス等の化石燃料を使用しないため、化石燃料の高騰によるアンモニア製造コストの上昇や、炭酸ガス排出による環境負荷がなく、しかも常温・常圧での合成であるため、エネルギー消費や設備規模が小さくて済み、経済性に優れている、アンモニアの合成方法を提供する。アンモニアの合成方法は、電解質相に、陽極と陰極とが所定間隔をおいて配置され、陽極ゾーンには、水が供給されるとともに、光が照射されて、光吸収反応により水が分解して、プロトン、電子および酸素ガスが形成され、陰極ゾーンには、窒素ガスが供給され、陽極ゾーンで生じた電子が、リード線を介して陰極ゾーンに移行せしめられて、陰極ゾーンにおいて N^{3-} が形成され、陽極ゾーンから電解質相内を陰極ゾーン側に移動してきたプロトンと、 N^{3-} との反応により、アンモニアが合成される。

DESCRIPTION

METHOD FOR SYNTHESIZING AMMONIA

TECHNICAL FIELD

The present invention relates to a method for synthesizing ammonia, and more particularly to a method for synthesizing ammonia which is capable of synthesizing ammonia without using a hydrogen gas.

BACKGROUND ART

Conventional ammonia synthesis processes use fossil fuels such as a natural gas as a hydrogen source that is a raw material for synthesis. Therefore, a rise in the ammonia production cost due to a steep rise in fossil fuel prices as well as environmental load due to carbon dioxide (CO₂) emissions have been a problem.

As a method for producing hydrogen without using fossil fuels, there are an electrolytic method using electrolysis of water, a photocatalytic degradation method for water by solar light, and a thermochemical method using solar heat and nuclear energy.

The Haber-Bosch process has been employed as a method for synthesizing ammonia using hydrogen. Here, the Haber-Bosch process is a method for synthesizing ammonia from a hydrogen gas and a nitrogen gas, and produces ammonia by reacting a

hydrogen gas with a nitrogen gas in the presence of an iron-based three-way catalyst.

The Haber-Bosch process is the mainstream of ammonia synthesis methods even at present because of its high synthesis efficiency, but the process has problems in that energy consumption and facility scale required are large because the process performs synthesis under high temperature and high pressure conditions, and that a large quantity of carbon dioxide (CO₂) is emitted in obtaining a hydrogen gas by steam reforming of hydrocarbons.

A method that does not require a hydrogen gas has been developed as a method for solving the above problems, and patent documents relating to such an ammonia synthesis method are as follows.

First, an electrolytic ammonia synthesis apparatus disclosed in Patent Document JP 2009-84615 is an apparatus for synthesizing ammonia from water and nitrogen, wherein the kind of steam to be supplied to an electrolytic bath and the means to agitate the electrolytic bath are devised. This electrolytic ammonia synthesis apparatus is characterized in that it is (1) an apparatus for synthesizing ammonia by supplying refined steam and N³⁻ to a molten salt being an electrolytic bath, and includes (2) a means for supplying a gaseous component to the molten salt and agitating the molten salt by a rising stream of the molten salt containing the gaseous

component, (3) an anode to generate an oxygen gas by oxidizing O^{2-} produced by the reaction of steam, and (4) a cathode to generate N^{3-} by the reduction of a nitrogen gas.

Here, the molten salt is at least one member selected from the group consisting of alkali metal halides and alkaline earth metal halides. In addition, the refined steam has a bubble diameter of 100 nm to 10 mm. Moreover, the refined steam is supplied so that the number of bubbles per 1 cm³ of the molten salt becomes 10 to 10000000.

Next, an ammonia synthesis apparatus disclosed in Patent Document JP 2005-27285 is characterized by including a mesh-like or porous cathode to which a nitrogen gas is supplied, a nitride solid electrolyte layer on the cathode, a mesh-like or porous anode provided on the nitride solid electrolyte layer, and a catalyst layer provided on the anode for adsorption and dissociation of hydrogen, and in which nitrogen negative ions are electrochemically generated in the nitride solid electrolyte layer by applying to the anode a positive electric potential with respect to the cathode; atomic nitrogen is obtained at the anode by oxidizing the nitrogen negative ions; and ammonia is synthesized at the anode by reacting atomic nitrogen with atomic hydrogen to be adsorbed and dissociated on the catalyst layer.

Since the ammonia synthesis apparatus disclosed in JP 2009-84615 uses an electrolytic bath of a molten salt made

from an alkali metal halide and an alkaline earth metal halide, the ammonia synthesis performed under a high temperature has a problem that consumption of the energy is very large. In addition, the ammonia synthesis apparatus described in JP 2005-272856 cannot solve the problem of use of a fossil fuel because a hydrogen gas must be supplied as a hydrogen source.

SUMMARY

At least one embodiment of the present invention may solve one or more of the above problems of the prior art, and may provide a synthesis method for ammonia, which may be capable of synthesizing ammonia without using a hydrogen gas, may be free from a rise in the ammonia production cost due to a steep rise of fossil fuel prices and from environmental load due to carbon dioxide (CO₂) emissions since the method may not use fossil fuels such as a natural gas as a conventional hydrogen source, and may be economical because energy consumption and facility scale required can be small since the synthesis may be performed at a normal temperature under a normal pressure.

The present inventors have found that ammonia can be synthesized by irradiating water with light in an anode zone to generate protons, electrons, and an oxygen gas due to decomposition of water by a photoabsorption reaction, allowing to transfer the electrons to a cathode zone to which a nitrogen gas is to be supplied to generate N³⁻ in the cathode zone, and

reacting this N^{3-} with the protons from the anode zone.

Disclosed herein is a method for synthesizing ammonia wherein an anode and a cathode are arranged in an electrolyte phase at a predetermined interval; a photocatalyst is provided to the anode; water (H_2O) is supplied to an anode zone and light is radiated so that water is decomposed by a photocatalytic reaction to generate protons (H^+), electrons (e^-), and an oxygen gas (O_2); a nitrogen gas (N_2) is supplied to a cathode zone, and the electrons (e^-) generated in the anode zone are allowed to transfer to the cathode zone through a lead, thereby generating N^{3-} in the cathode zone; and ammonia (NH_3) is synthesized through the reaction between the protons (H^+) that have moved toward the cathode zone from the anode zone in the electrolyte phase and N^{3-} ; and wherein the anode is a substrate made of indium tin oxide (ITO) or fluorine tin oxide (FTO); the cathode is a Ni porous body, a nickel-, iron-, or ruthenium-loaded Ni porous body, carbon paper, or nickel-, iron-, or ruthenium-loaded carbon paper; and the photocatalyst is a visible light-responsive photocatalyst comprising an oxynitride compound, an oxysulfide compound, or an oxide containing metal ions of d^{10} electron state.

In one embodiment the light to be radiated to the anode zone is solar light, or visible light emitted from a light irradiation lamp.

As set forth above, the ammonia synthesis method

comprises an anode and a cathode are arranged in an electrolyte phase at a predetermined interval; a photocatalyst is provided to the anode; water (H_2O) is supplied to an anode zone and light is radiated so that water is decomposed by a photocatalytic reaction to generate protons (H^+), electrons (e^-), and an oxygen gas (O_2); a nitrogen gas (N_2) is supplied to a cathode zone, and the electrons (e^-) generated in the anode zone are allowed to transfer to the cathode zone through a lead, thereby generating N^{3-} in the cathode zone; and ammonia (NH_3) is synthesized through the reaction between the protons (H^+) that have moved toward the cathode zone from the anode zone in the electrolyte phase and N^{3-} . In accordance with at least one embodiment of the invention, it may be possible to synthesize ammonia without using a hydrogen gas. Therefore, embodiments of the present invention may be free from a rise in the ammonia production cost due to a steep rise of fossil fuel prices and from environmental load due to carbon dioxide (CO_2) emissions since the method does not use fossil fuels such as a natural gas as a conventional hydrogen source, as well as that the method may be excellent in economy because energy consumption and facility scale required are small since the synthesis is performed at a normal temperature under a normal pressure. Further, using the methods of some embodiments in accordance with the invention it may be possible to synthesize ammonia with high efficiency using the photocatalyst because the water

decomposition reaction proceeds fast.

As set forth above, in one embodiment the light to be radiated to the anode zone may be solar light, or visible light emitted from a light irradiation lamp. In this respect it may be possible to synthesize ammonia with high efficiency by using solar light, or visible light emitted from a light irradiation lamp because such light can have a high energy so that the water decomposition reaction proceeds fast with the light.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a flow sheet showing an embodiment of an apparatus for performing the ammonia synthesis method according to an embodiment of the present invention.

DETAILED DESCRIPTION

Next, an embodiment of the present invention will be explained with reference to the drawing, but the present invention is not limited thereto.

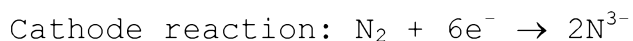
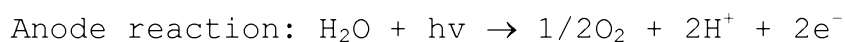
Fig. 1 shows a specific example of an apparatus for performing the ammonia synthesis method according to an embodiment of the present invention. Referring to the drawing, in the ammonia synthesis method according to the embodiment of the present invention, an anode and a cathode are arranged in an electrolyte phase at a predetermined interval.

In an anode zone, water (H_2O) is supplied and light is

radiated so that a photoabsorption reaction takes place to decompose water, thereby generating protons (H^+), electrons (e^-), and an oxygen gas (O_2).

In a cathode zone, a nitrogen gas (N_2) is supplied; the electrons (e^-) generated in the anode zone are allowed to transfer to the cathode zone through a lead, thereby generating N^{3-} in the cathode zone; and ammonia (NH_3) is synthesized through the reaction between the protons (H^+) that have moved toward the cathode zone from the anode zone in the electrolyte phase and N^{3-} .

In the ammonia synthesis method according to the embodiment of the present invention, the chemical reactions in the anode zone and the cathode zone are as follows:



Using the ammonia synthesis method according to the embodiment of the present invention, it may be possible to synthesize ammonia without using a hydrogen gas. In addition, the method is free from a rise in the ammonia production cost due to a steep rise of fossil fuel prices as well as environmental load due to carbon dioxide (CO_2) emissions since the method does not use fossil fuels such as a natural gas as a conventional hydrogen source, and the method is also excellent in economy because energy consumption and facility scale required are

small since the synthesis is performed at a normal temperature under a normal pressure.

In the ammonia synthesis method according to the embodiment of the present invention, it is preferable that a photocatalyst is provided to the anode and light is radiated to the anode zone so that a photocatalytic reaction takes place to decompose water, thereby forming protons, electrons, and an oxygen gas.

Here, it is preferable to use an anode substrate made of indium tin oxide (ITO), fluorine tin oxide (FTO), or the like.

In addition, it is preferable to use, as a cathode, for example, a Ni porous body, a nickel-, iron-, or ruthenium-loaded Ni porous body, carbon paper, or nickel-, iron-, or ruthenium-loaded carbon paper.

The photocatalyst may be a so-called visible light-responsive photocatalyst so long as it exerts a photocatalytic activity with visible light. Such a visible light-responsive photocatalyst may be, for example, an oxynitride compound typified by TaON, LaTiO₂N, CaNbO₂N, LaTaON₂, or CaTaO₂N; an oxysulfide compound typified by Sm₂Ti₂S₂O₇; or an oxide containing metal ions of d¹⁰ electron state, which is typified by CaIn₂O₄, SrIn₂O₄, ZnGa₂O₄, or Na₂Sb₂O₆.

By using these photocatalysts, the water decomposition reaction proceeds fast, thereby enabling to produce ammonia with high efficiency.

In the ammonia synthesis method according to the present invention, it is preferable that light to be radiated in an anode zone is solar light, or visible light emitted from a light irradiation lamp. Here, as the light irradiation lamp, for example, a xenon lamp or a krypton lamp is preferably used. Again, ammonia can be synthesized with high efficiency by using such visible light because the light has the highest energy, and the water decomposition reaction proceeds fast.

EXAMPLES

Hereinafter, an example of an embodiment according to the present invention will be explained, but the present invention is not limited thereto.

Example 1

First, 0.002 N aqueous solution of sulfuric acid (H_2SO_4) was used as an electrolyte of an electrolyte phase. Indium tin oxide (ITO) was used as a substrate for an anode, and a visible light-responsive photocatalyst TaON as a photocatalyst was loaded onto an ITO substrate by application. In addition, a Ni porous body was used as a cathode.

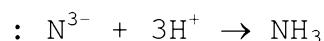
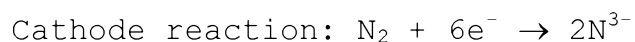
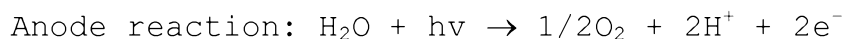
Then, in the electrolyte phase, the anode provided with the photocatalyst and the cathode were arranged at a predetermined interval, and visible light was radiated at 300 W with a xenon lamp in an anode zone while supplying water (H_2O). By this procedure, water was decomposed by a photocatalytic

reaction in the anode zone, thereby generating protons (H^+), electrons (e^-) and an oxygen gas (O_2).

Meanwhile, a nitrogen gas (N_2) was circulated at a flow rate of 100 ml/min in a cathode zone.

A voltage of 2.8 to 3.4 V was applied between the electrodes, and an ionic conductivity at that time of the electrolyte was measured. By this procedure, electrons (e^-) generated in the anode zone were allowed to transfer to the cathode zone through a lead; N^{3-} was generated in the cathode zone by reception of electrons (e^-) by a nitrogen gas (N_2); and ammonia (NH_3) was generated through the reaction between the protons (H^+) that had moved toward the cathode zone from the anode zone in the electrolyte phase and N^{3-} . The generated ammonia was emitted from the apparatus together with the nitrogen gas that was circulated in the cathode zone.

In the ammonia synthesis method according to the example of the present invention, the chemical reactions in the anode zone and the cathode zone were as follows:



As a result, the ionic conductivity of the electrolyte phase of the aqueous sulfuric acid solution after the ammonia synthesis reaction was reduced to 0.50 mS/cm while the ionic conductivity of the electrolyte phase of the aqueous sulfuric

acid solution before the initiation of the ammonia synthesis reaction was 0.84 mS/cm, indicating that ammonia was generated.

The above references to the background art do not constitute an admission that the art forms part of the common general knowledge of a person of ordinary skill in the art. The above references are also not intended to limit the application of the method as disclosed herein.

In the claims which follow, and in the preceding description, except where the context requires otherwise due to express language or necessary implication, the word "comprise" and variations such as "comprises" or "comprising" are used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the method as disclosed herein.

CLAIMS

1. A method for synthesizing ammonia, wherein an anode and a cathode are arranged in an electrolyte phase at a predetermined interval; a photocatalyst is provided to the anode; water (H_2O) is supplied to an anode zone and light is radiated so that water is decomposed by a photocatalytic reaction to generate protons (H^+), electrons (e^-), and an oxygen gas (O_2); a nitrogen gas (N_2) is supplied to a cathode zone, and the electrons (e^-) generated in the anode zone are allowed to transfer to the cathode zone through a lead, thereby generating N^{3-} in the cathode zone; and ammonia (NH_3) is synthesized through the reaction between the protons (H^+) that have moved toward the cathode zone from the anode zone in the electrolyte phase and N^{3-} ; wherein the anode is a substrate made of indium tin oxide (ITO) or fluorine tin oxide (FTO); the cathode is a Ni porous body, a nickel-, iron-, or ruthenium-loaded Ni porous body, carbon paper, or nickel-, iron-, or ruthenium-loaded carbon paper; and the photocatalyst is a visible light-responsive photocatalyst comprising an oxynitride compound, an oxysulfide compound, or an oxide containing metal ions of d^{10} electron state.

2. A method for synthesizing ammonia according to claim 1, wherein the light to be radiated to the anode zone is solar light, or visible light emitted from a light irradiation lamp.

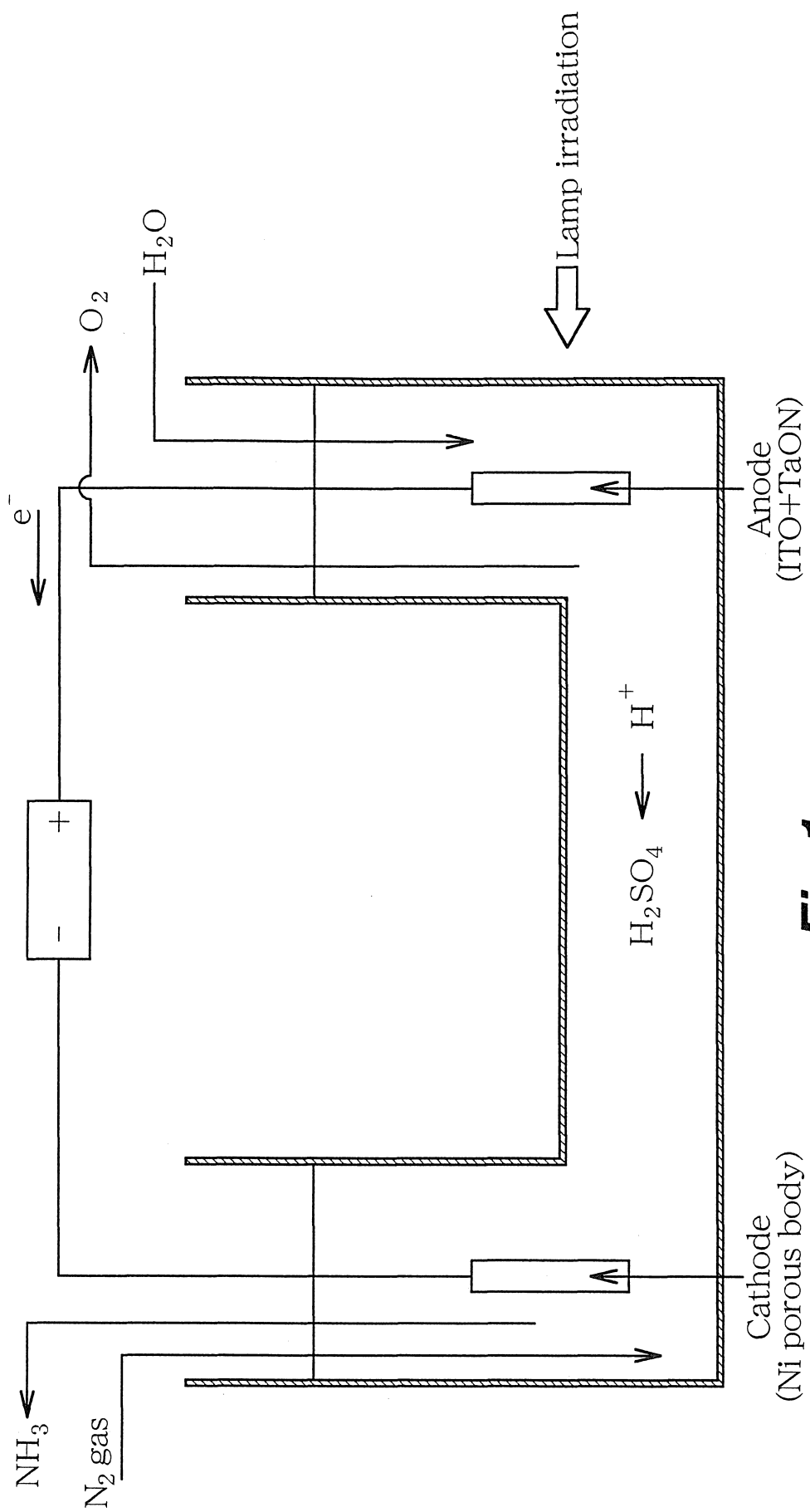


Fig.1